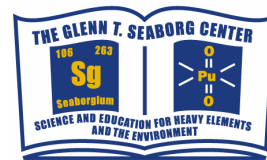




Technetium Chemistry in Waste Environments



Wayne Lukens
David Shuh

Environmental Management
Science Program
High-Level Waste Workshop

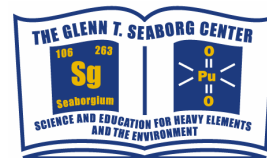
January 20, 2005



Inside tank SY-101, the
“hydrogen burping tank”



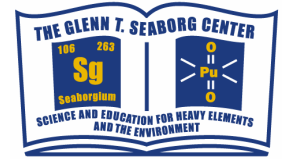
Acknowledgements



- Technetium Chemistry: Norman Schroeder, Kenneth Ashley
- Radiation Chemistry: Don Camaioni, Dan Meisel, Dieter Asmus
- Grout Components: Christine Langton
- Glass: Ian Pegg, David McKeown, Isabelle Muller
- EXAFS: Corwin Booth, David Shuh
- This work was supported by the Office of Science and Technology, within the U.S. Department of Energy, under the Office of Environmental Management's Science Program at the Ernest O. Lawrence Berkeley National Laboratory under Contract No. DE-AC03-76SF00098.
- This work was performed, in part, at the SSRL, which is operated by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Division of Chemical Sciences.



Outline



Introduction: Why do we care about technetium?

Behavior of technetium in high level waste

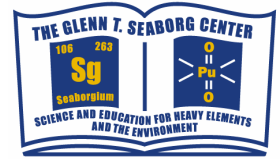
- Radiolysis of pertechnetate
- Identification of nonpertechnetate species at Hanford

Behavior of technetium in waste forms

- Technetium species formed in reducing grout
- Oxidation of technetium species in reducing grout
- Speciation of technetium in glass



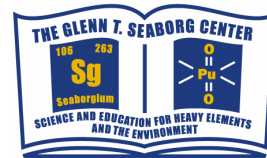
Technetium Background



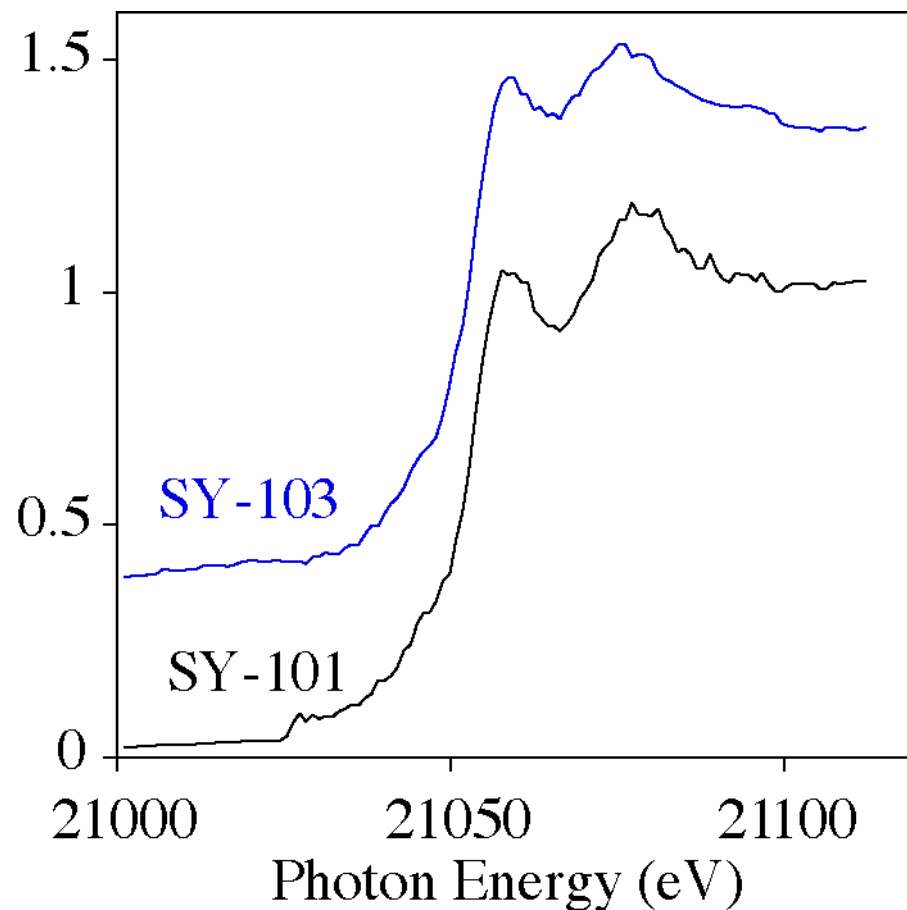
- Long lived: $\tau_{1/2} = 213,000$ yr for ^{99}Tc
- Abundant fission product: 6% yield from ^{235}U fission
 - Approximately 1600 kg ^{99}Tc at Hanford
 - Approximately 3500 kg ^{99}Tc at Savannah River
- Moderately radiotoxic (^{99}Tc)
 - β -emitter (< 300 keV)
 - Does not bioaccumulate in animals
- Very important in performance assessments
 - TcO_4^- has high environmental mobility



Soluble Lower Valent Tc Created Problems at Hanford



- 80% of Tc needed to be removed from the supernate.
- Soluble Tc species cannot be removed by ion exchange used to.
- Identity is unknown, thought to be Tc(IV).

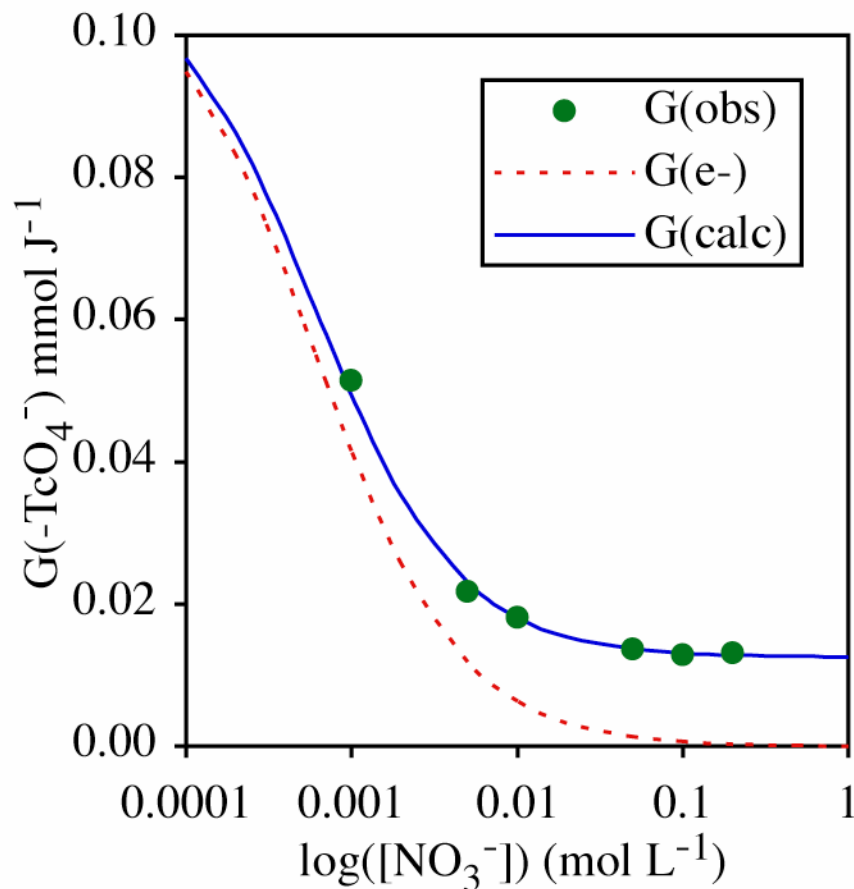
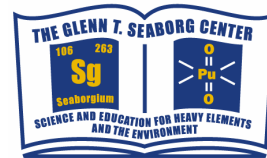


—Schroeder, et al. *LA-UR-95-4440*, Los Alamos National Lab, Los Alamos, NM

—Blanchard, et al. *PNNL-11386*, Pacific Northwest National Lab, Richland, WA



Radiolytic Reduction of TcO_4^- in the Presence of Excess Nitrate

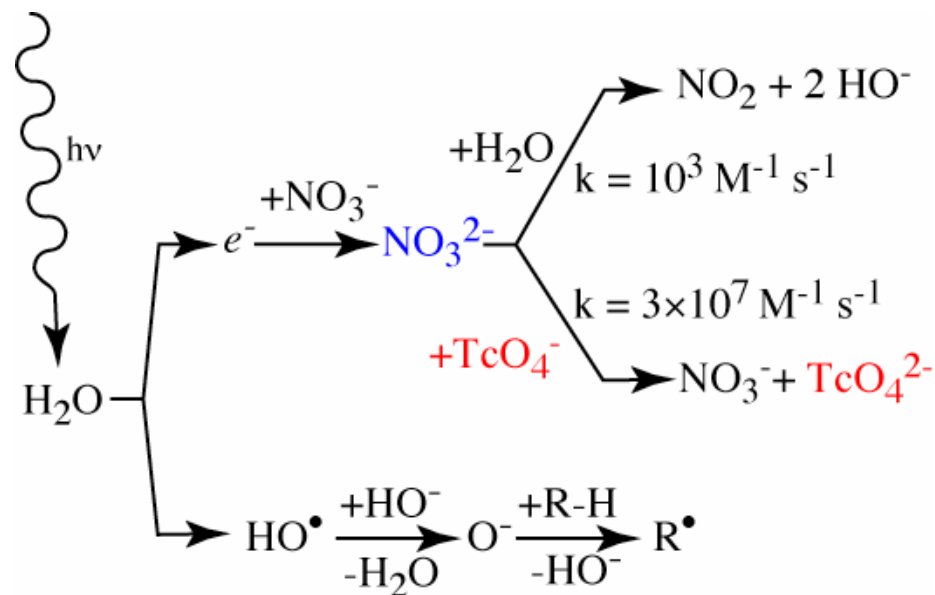


- Potential reductant: NO_3^{2-}

$$— E^0(\text{NO}_3^-/\text{NO}_3^{2-}) \bullet -1.0 \text{ V}$$

$$E^0(\text{TcO}_4^-/\text{TcO}_4^{2-}) = -0.68 \text{ V}$$

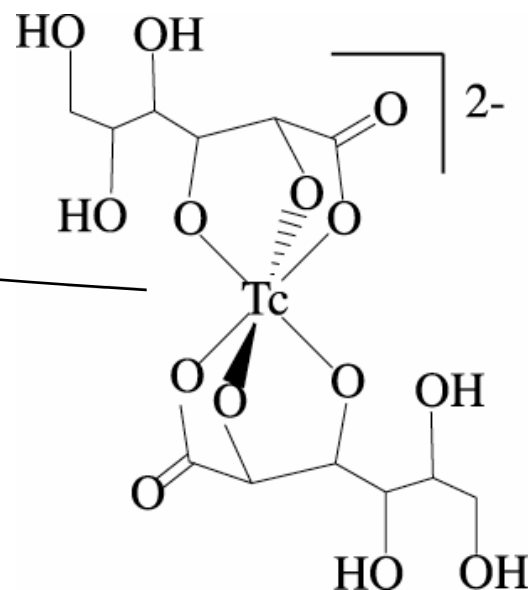
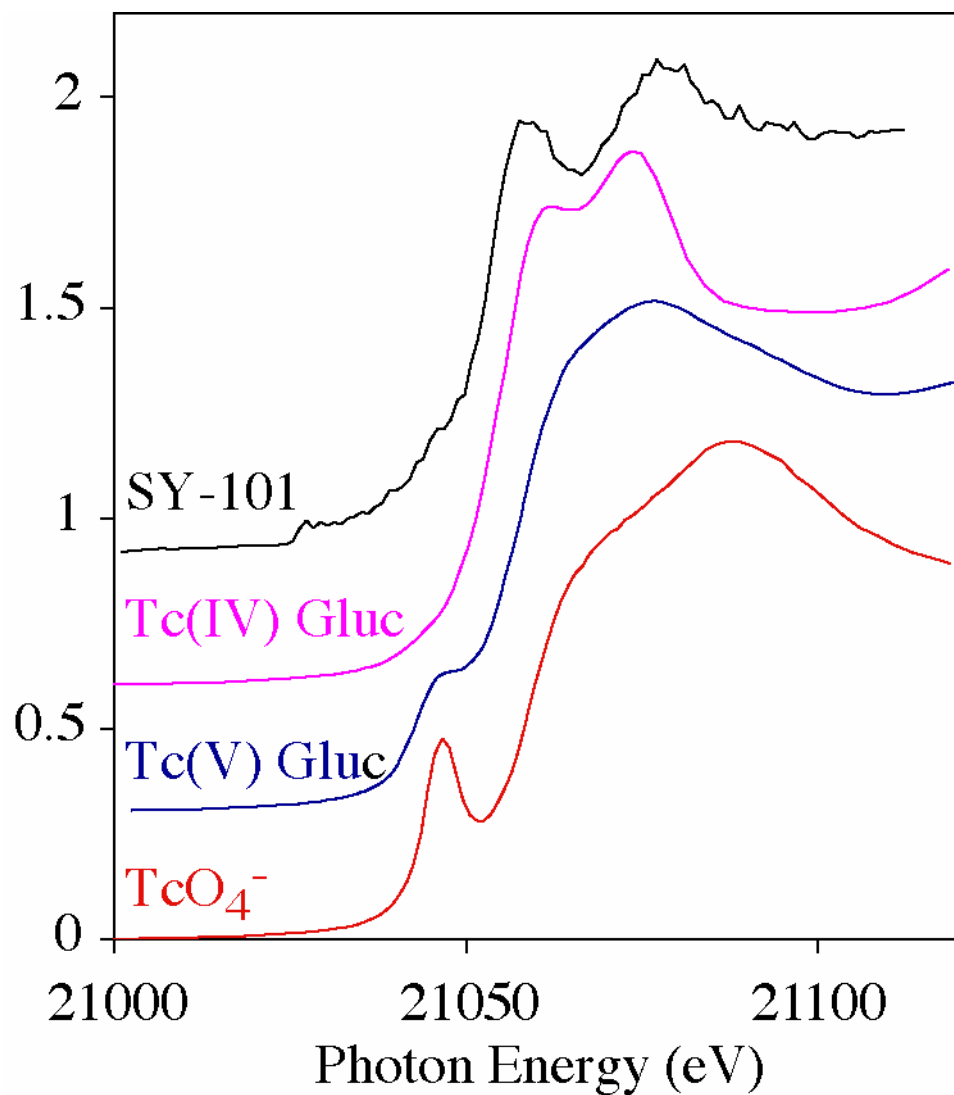
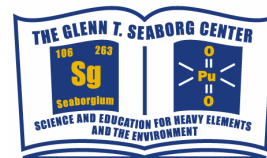
- Mechanism:



- *J. Phys. Chem. A* **2001**, 105, 9611-9615

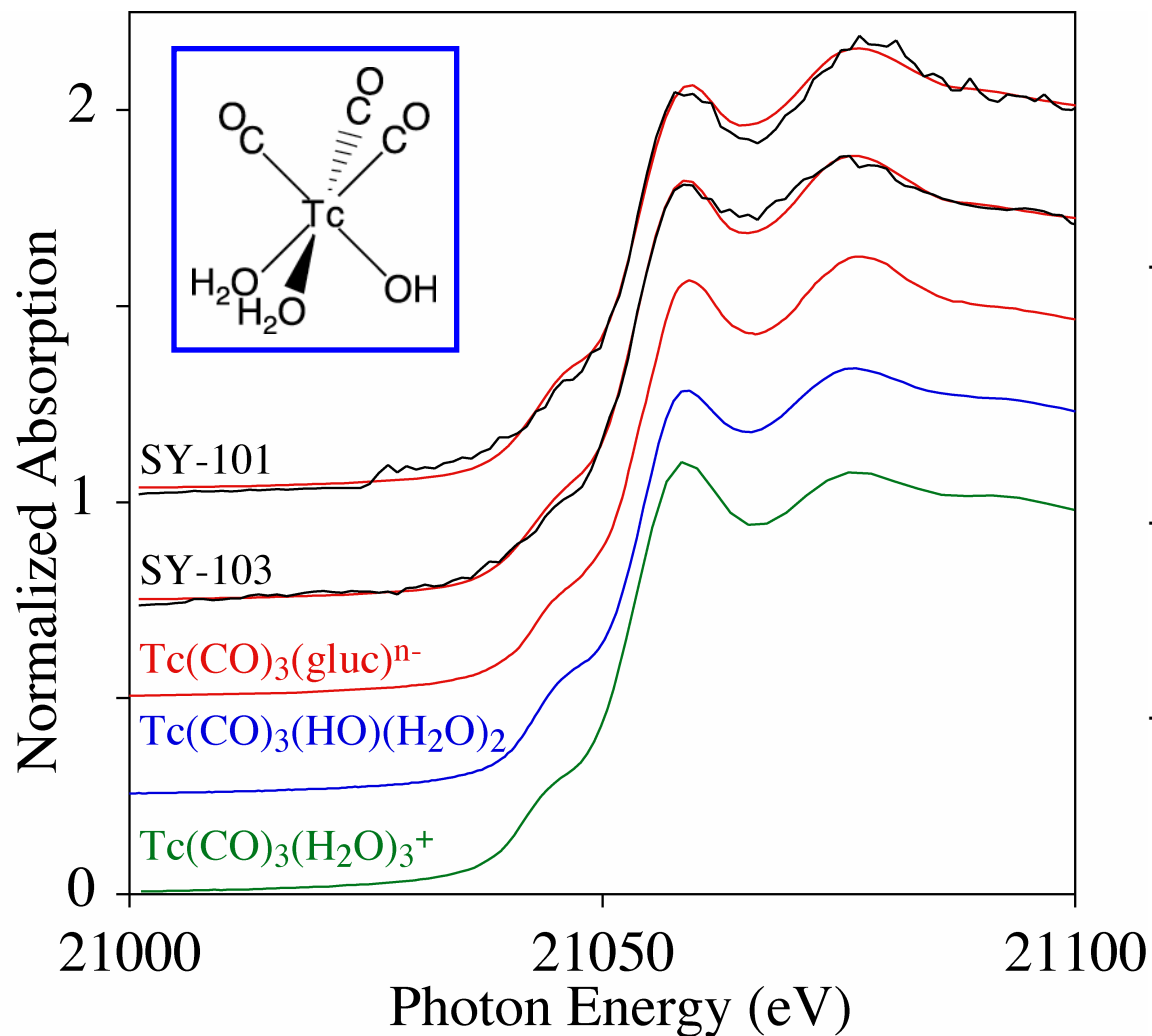
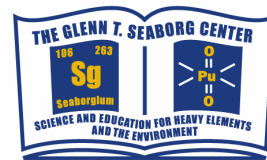


XANES Spectrum of Tc(IV) Gluconate





XANES Spectra of Tc(I) Carbonyl Complexes



XANES results

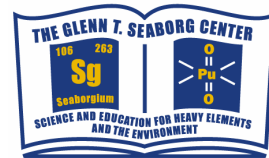
- both $\text{Tc(CO)}_3(\text{H}_2\text{O})_2(\text{HO})$ and $\text{Tc(CO)}_3(\text{gluconate})^{2-}$ fit the data
- fit is slightly better with $\text{Tc(CO)}_3(\text{gluconate})^{2-}$
- $\text{Tc(CO)}_2(\text{NO})$ also possible

- *Environ. Sci. Technol.*, **2004**, 38, 229-233



Summary

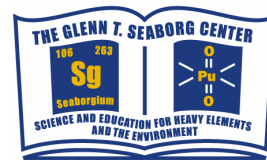
(Technetium in High Level Waste)



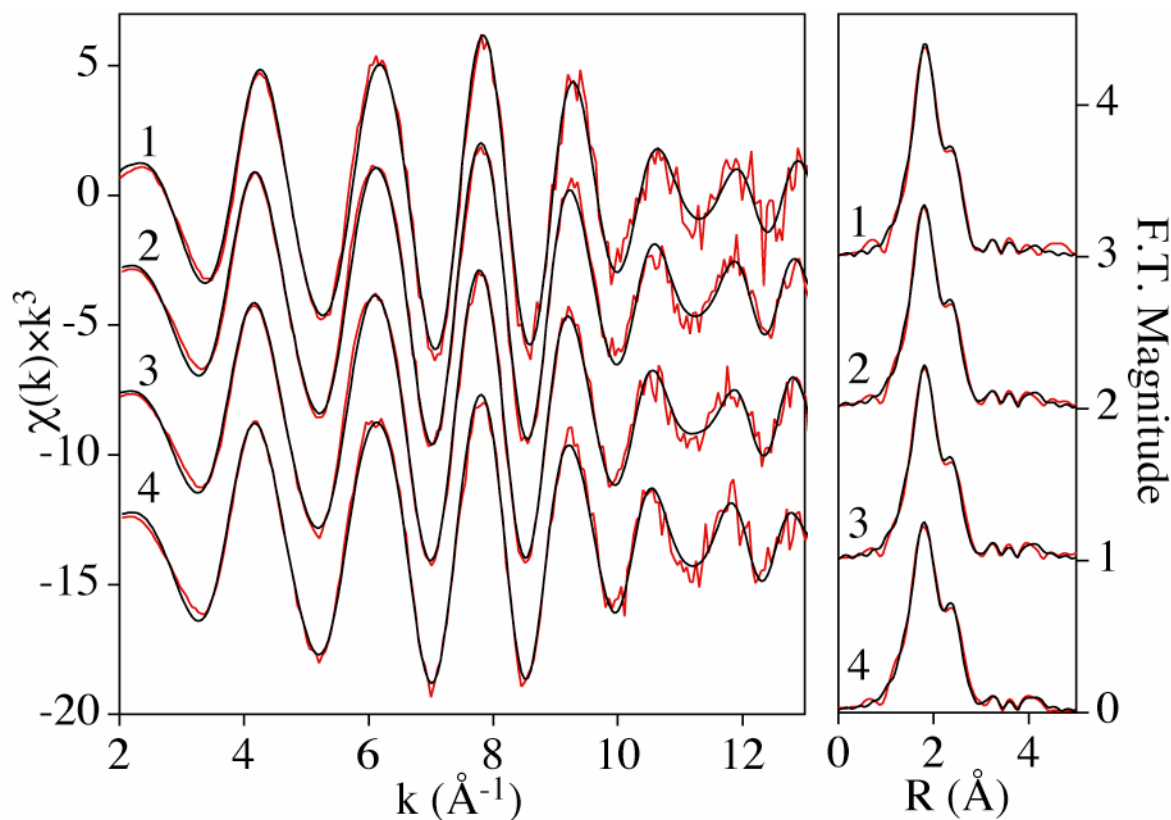
- TcO_4^- can be reduced by radiolysis
 - Actual reducing agent is NO_3^{2-}
 - A scavenger for O^- is necessary (nitrite)
- The soluble species are Tc(I) carbonyl complexes
 - Tc(IV) alkoxides may also be present
 - *Environ. Sci. Technol.*, **2002**, 36, 1124-1129



Initial Speciation of Technetium in Reducing Grout

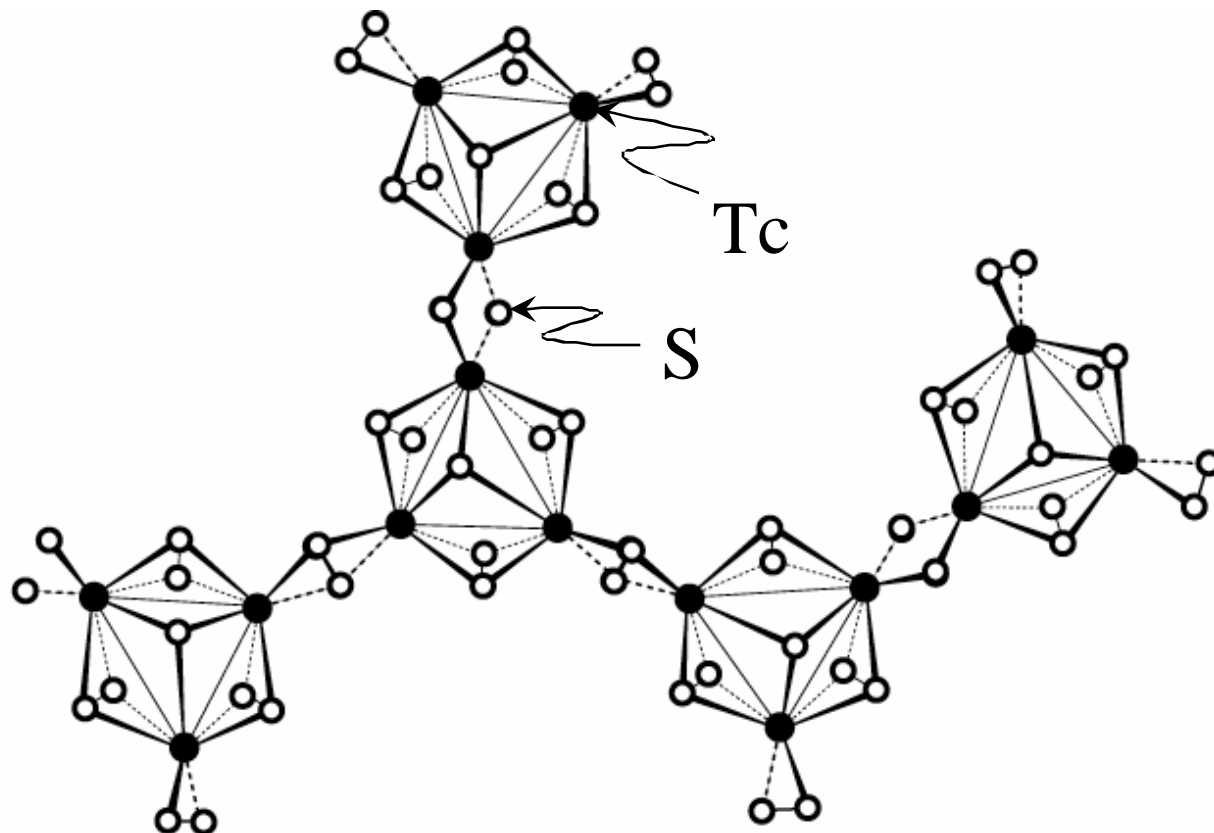


Tc K-edge EXAFS



Scattering Atom		Sample 1
S	N	7.4(2)
	R	2.367(2)
	σ^2	0.0108(4)
Tc	N	2.1(1)
	R	2.767(2)
	σ^2	0.0073(6)
Tc	N	0.22(8)
	R	3.82(2)
	σ^2	0.003(1)
Tc	N	0.78 ^a
	R	4.28(1)
	σ^2	0.003 ^a
S	N	2.5(5)
	R	4.41(2)
	σ^2	0.005 ^b
ΔE_0		-7.1(4)

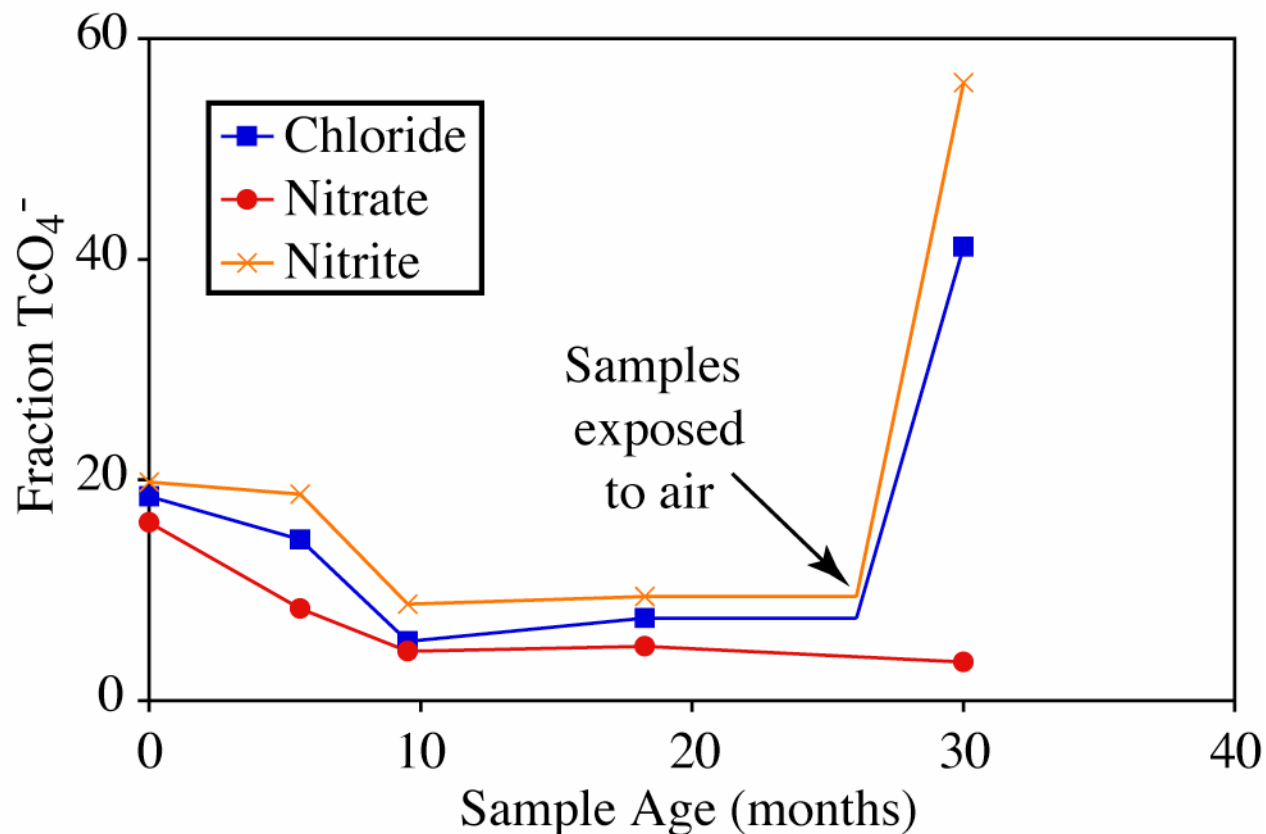
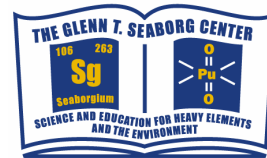
Structural Model for “Tc₂S₇”



- Similar to MoS₃
- Formula: Tc₃S₁₀
- Tc₃S₁₀ is Tc(IV)



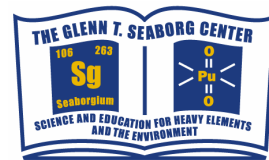
Oxidation of Tc(IV) in Reducing Grout by O₂



- $D_{\text{eff}}(\text{NO}_3^-) = 9.5 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$
 - Smith, R. W.; Walton, J. C. *Mat. Res. Soc. Symp. Proc.* **1993**, 294, 247.



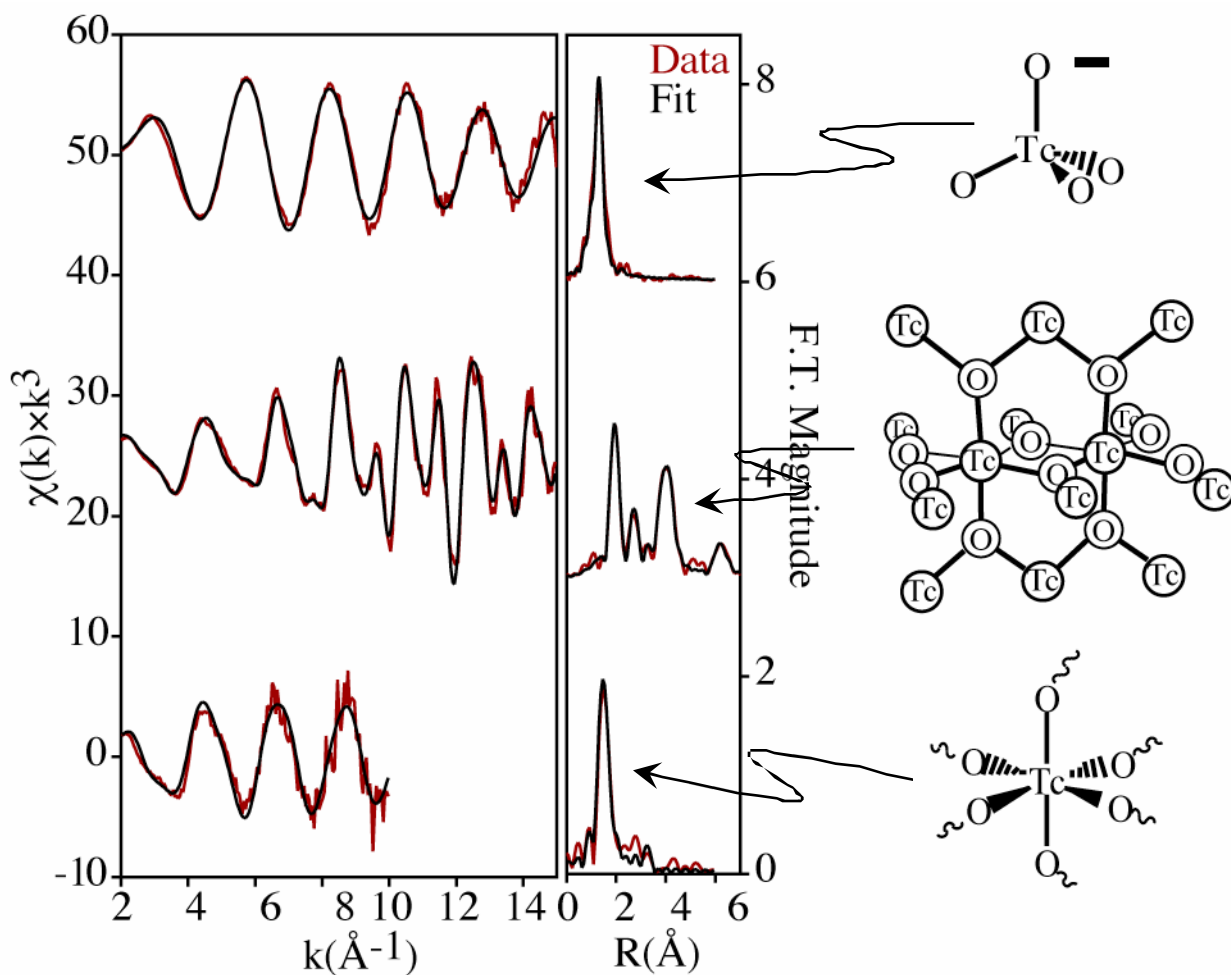
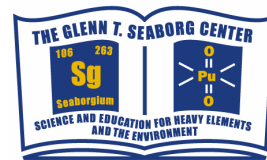
Summary (Grout)



- “ Tc_2S_7 ” is the Tc(IV) disulfide compound Tc_3S_{10}
- Tc(IV) in grout is air sensitive
- Rate of oxidation is consistent with the “shrinking box” model of Smith and Walton
- Tc(IV) in grout is not oxidized by nitrate (on these time scales)



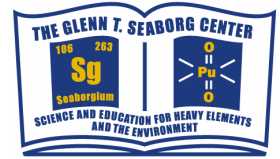
Speciation of Technetium in Glass (Hanford LAW)



- *Mat. Res. Soc. Symp. Proc.* **2004**, 802, 101-106



Current and Future Work



- Comparison of the behavior of Tc and Re in glass
- Tc volatility during vitrification
- Materials that adsorb TcO_4^- (especially at high pH)